Dynamic-mechanical analysis and SEM morphology of wood flour/polypropylene composites

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Abstract: A study was conducted to investigate the effects of compatibilizers, including Maleic anhydride grafted polypropylene (MA-PP) and maleic anhydride grafted ethylene-propylene-diene copolymer (MA-EPDM), on wood-flour/polypropylene (WF/PP) composites. WF/PP composites were prepared by direct extrusion profiles using a twin-screw/single-screw extruder system. DMA analysis showed that the loss factor of composites decreased and the storage modulus improved in the presence of MA-PP, which indicated much better interfacial adhesion between the PP matrix and wood flour filler than in the absence of compatibilizer. Morphological feature based on SEM observation showed that MA-PP and MA-EPDM improved the dispersion of the wood particles in the plastic matrix. MA-EPDM is a soft segment, although it improved the interfacial adhesion, storage modulus decreases with adding of MA-EPDM. As compatibilizer of wood-flour/polypropylene composites, both DMA analysis and SEM feature proved that MA-PP was superior to MA-EPDM.

Key words: Wood flour; Polypropylene; Composites; Dynamic-mechanical analysis

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Introduction

It is well known that over the past few decades, polymers have replaced many conventional materials, such as metal and wood in many applications. This is due to the advantages of polymers over conventional materials (Maurizio *et al*. 1998; Adrian *et al*. 2003). Recently, natural fiber reinforced polymer attracted the attention of researchers because of its advantages over its established materials. Plant fibers are biodegradable and easy available, with the performances of low cost, low density, lower abrasive nature comparing with glass-fibers (Georgopoulos *et al*. 2005; Ismail *et al*. 2001; Wielage *et al*. 2003). However, poor compatibility with the hydrophobic polymer matrix and the tendency to form aggregates during the processing and the low resistance to moisture, greatly reduce the potential of natural fibers to be used as reinforcement for polymers (Velichko *et al*. 2003; Hristov *et al*. 2004a; Fernanda *et al*. 2000). Rajeev *et al*. (1997) reported that the properties of wood-fiber/polypropylene (WF/PP) composites were very poor due to the absence of interfacial modifiers.

There is an increasing interest in using non-wood based materials because of the diminishment of wood resources all over the world. China has a large quantity of natural fiber generated from wood industries such as wood flour (Torres *et al*. 2005; Wu *et al*. 2005). Wood flour/thermoplastic composites have the performances of environmental protection and economical advantages, and may play an important role in resolving future environmental problems arising from solid wastes of wood and plastic products. Hence, Wood-flour/thermoplastic is considered a new way to effectively utilize wood resource (Joao *et al*. 2003; Hristov *et al*. 2004b, 2004c; Kristiina *et al*. 2003).

Generally, the thermoplastic matrix and wood flour do not react each other strongly, resulting in poor stress transfer along the interface (Krzysik *et al*. 1990). Many studies were conducted on seeking new ways to couple the two phases and how to enhance the interfacial compatibility to increase the mechanical and physical properties of wood-fiber/polypropylene (WF/PP) composites. However, owing to the complexity of interface status, the advance of research progress for interface compatibility was very slow (David *et al*. 2004; Lu *et al*. 2000).

In this study we used a thermoplastic polymer, polypropylene (PP), as the matrix and maleic anhydride grafted polypropylene (MA-PP) or maleic anhydride grafted ethylene-propylene-diene copolymer (MA-EPDM) as compatibilizer to study the interface compatibility between wood flour and polypropylene. WF/PP composites were prepared by a twin-screw/single-screw extruder system, analyzed by dynamic mechanical analysis (DMA), and observed by scanning electron microscope (SEM).

Material and methods

Materials

Polypropylene (Density 0.89–0.91 g·cm^{-3}, the melting flew index of 8 g per 10 min) used as the matrix of the composites was supplied by Daqing Petrochemical Company, China. Wood flour (20–240 mesh) with 8% of moisture content was supplied by Harbin Yongxu Co. Ltd. MA-PP with grafting ratio 1.8% and MA-EPDM with grafting ratio 0.8% used as compatibilizer and coupler for wood flour /polypropylene composites were supplied by Guangzhou Bochen Co. Ltd.

Instruments

SJSH30 mm twin-screw/45 mm single-screw extruder system (Nanjing Rubber & Plastic Machinery Co. Ltd.), Netzsch Geratebau GmbH DMA242 (Germany), FEI QuanTa200 SEM (Holand) were used in this experiment.

Preparation of composites

Wood flour were dried at 105°C for 24 h for removing moisture, and then stored over in sealed containers. In order to study the effect of the addition of compatibilizer including MA-PP or

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MA-EPDM on the properties of WF / PP, a fixed ratio of amount of WF / PP and WF / PP as 40: 60 was employed. WF / PP(PW), WF /PP and 2% MA-PP (PWM2), WF / PP and 5% MA-PP (PWM5),WF / PP and 8% MA-PP (PWM8) ,WF / PP and 5% MA-EPDM (PWE5), WF / PP and 8% MA-EPDM (PWE8),WF / PP and 10% MA-EPDM (PWE10) were used. WF, PP and additives were mixed in a high speed mixer for 8 min, subsequently melted and extruded by the twin-screw/single-screw extruder system. The processing temperature for extrusion was set at 150°C for melting zone, 170–180°C for pumping zone, and 175°C for die zone, respectively. The rotary speed of twin-screw was 100 rpm.

Dynamic mechanical analysis of composites

Dynamic mechanical analysis (DMA) was performed with rectangular measuring system using a three-point bending, which only required samples with small mass or small size. Rectangular specimens were cut from the pressed sheet to the size of 50mm×10 mm×3 mm. The specimen were measured using DMA242 (Germany) to obtain the curves of storage modulus (E′) and loss factor (tanδ) at the fixed frequency of 1 Hz and temperature ranging from –100°C to 200°C, at a heating rate of 3°C·min^{-1} under a flow of nitrogen.

Morphological study

The morphology of composites was examined using a scanning electron microscope (SEM). The fracture surface of the sample was sputter-coated with gold-palladium alloy before examination. SEM micrograph magnifications were ×5 000 and ×10 000.

Results and discussion

Temperature-dependent DMA measurements

Dynamic-mechanical analysis (DMA) has been a well established method in thermal analysis. The DMA measurement consists of the observation of time-dependent deformation behavior of a sample under periodic mostly sinusoidal deformation force with very small amplitudes. Thus it is possible to calculate storage modulus E′ and loss factor tanδ in dependence on temperature and deformation frequency. The temperature curves of storage modulus (Fig.1) reveal the differences between the pure polymer matrix and a composites system with MA-PP. From Fig.1, we can see that there is an initial decrease in storage modulus as MA-PP content increases from 0 to 2% parts, the initial reduction of E′ is presumed due to WF/PP incompatibility, which shows that the addition of a low percentage of MA-PP is not sufficient to form a good wetting. With MA-PP content between 5% and 8%, the storage modulus E′ reaches higher values, which indicates an enhanced stiffness. For example, at 50°C, E′ increases from 5 500 to 7 500 MPa, which was considered to be due to the better compatibility between WF and PP, and less mobility of PP segments. The results indicated that incorporation of WF in the PP matrix with MA-PP improved the stiffness of the composites.

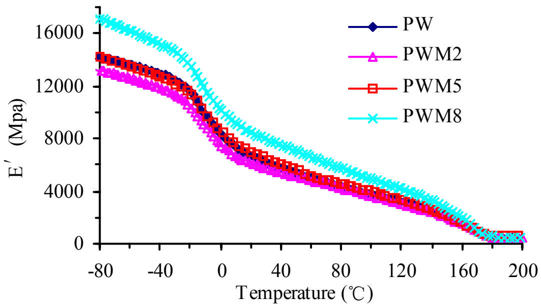

Fig. 1 Influence of MA-PP content on storage modulus E

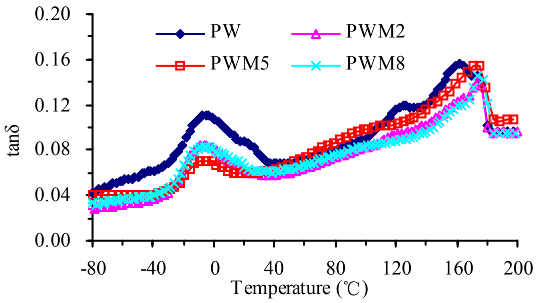

Fig. 2 Influence of MA-PP on loss factor tanδ

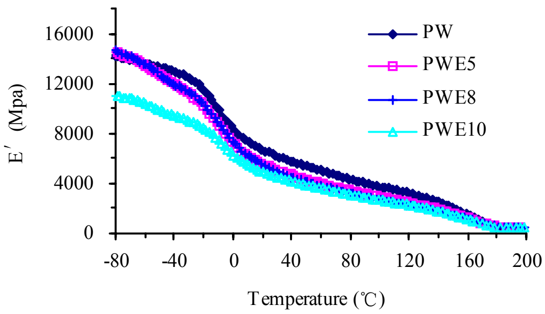

Fig. 3 Influence of MA -EPDM content on storage modulus E′

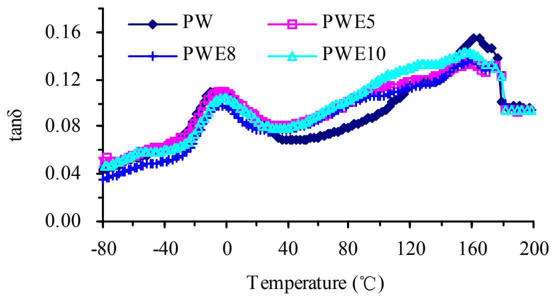

Fig. 4 Influence of MA - EPDM on loss factor tanδ Morphological observations

McGrumet *et al.* (1967) reported that the tanδ curve of PP exhibits three relaxations localized in the vicinity of –80°C (γ), 10°C (β) and 100°C (α). In the present work, the study mainly focused on the β-relaxation of PP that corresponded to the glass rubber transition of the amorphous portion and the temperature at the maximum peak is assigned to the glass transition temperature (T_g). Within a temperature range from –20°C to 10°C, E′ rapidly decreases with temperature rising, and tanδ forms a peak. The temperature corresponding to the peak is considered to be T_g.

The temperature curve of loss factor tanδ (Fig. 2), an impor-

tant parameter characterizing material viscoelasticity, indicates a relaxation process. With increasing MA-PP, relatively lower values of the maximum tanδ are observed. Ashida *et al.* (1985) reported the relation between tanδ and interface adhesion. It can indirectly show the interface adhesion property, the smaller the loss factor tanδ, the better the interface adhesion. When the temperature is below the glass transition, where molecules chains lose mobility, the tanδ is lower. When the temperature in the range corresponding to glass transition of the polymer, where molecules regained their mobility, the glass transition area is indicated by the maximum of tanδ at around –10°C. Tanδ is influenced by the type of matrix, wood flour content, compatibilizer, and processing parameters.

The influences of MA-EPDM on storage modulus and loss factor are separately shown in Fig. 3 and Fig. 4. Tanδ has not change much and we can not draw any clear conclusions regarding the influence of MA-EPDM contents, this implies that the adjustable factors such as rotor speed, processing temperature, and mixing time need not to be change during processing as the MA-EPDM content increased. Lower stiffness values (or storage modulus) at the MA-EPDM composites are obtained, with an amount of adding to the composites, the material exhibits a low storage modulus, and loss factor changes very small. It shows that there is an insufficient wetting between WF and PP, but it is better than no compatibilizer. By comparing with Fig. 1 and Fig. 3, we found that when adding the same content compatibilizer (e.g. 8%), the storage modulus containing MA-PP is higher than that of containing MA-EPDM, which shows that MA-PP improves the interface adhesive of WF and PP. These results are in agreement with the microphotographs taken in the SEM and reported in Figs. 5–6.

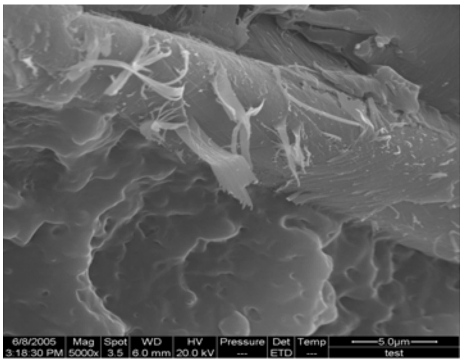

Fig. 5 SEM micrographs of the fracture surface with 10 percent MA-EPDM ×5000

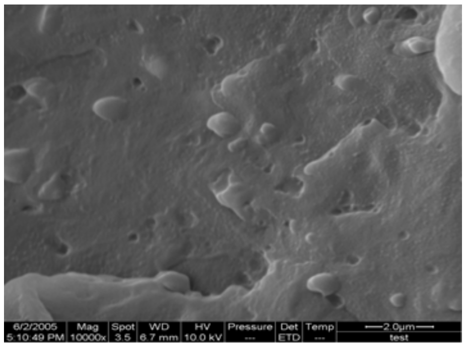

Fig. 6 SEM micrographs of the fracture surface with 10 percent MA-EPDM ×10000

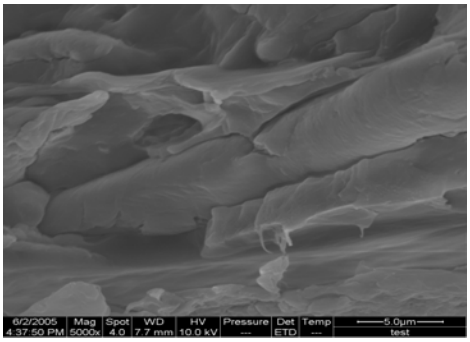

Fig. 7 SEM micrographs of the fracture surface without compatibilizer

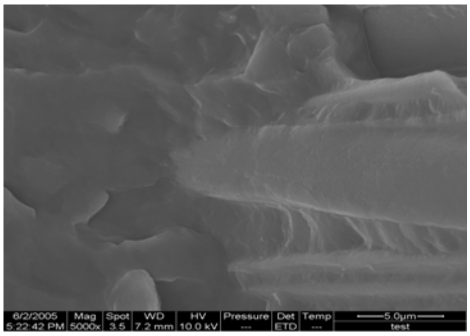

Fig. 8 SEM micrographs of the fracture surface with 5 percent MA-PP

Fig.7 shows the tensile fracture surfaces of composites without compatibilizer. The pulled-out traces of WF can be seen in the SEM micrographs, which indicate poor adhesion between the matrix and wood flour. When the MA-PP is added to the composite, WF is covered by a layer of the matrix PP that has been pulled out together with the WF, which indicates the interfacial adhesion is noticeably improved (Fig. 8). MA-PP causes a significantly better wetting of WF and PP than without its use. PP covering WF changes the local stress distribution. This means a better stress transfer and superior impact strength could be obtained. It contributes to an optimal interfacial bond between the WF/PP. High quality bonding between wood flour and PP retards WF pulling out of PP matrix and the fracture path passes from the matrix through the interface and wood flour. Obviously, the compatibilizer contributes to the formation of a strong interfacial layer, which alters the local stress distribution and makes the deformation and fracture mechanism change. In Fig.5 the fracture surface of the MA-EPDM added wood-flour/PP composites is shown. EPDM elastomer particles are dispersed in the matrix and this dispersion of the elastomer improves the impact strength of composites by absorbing energy through deformation. The compatibilizing effect leads to a decrease in the size of phases and an increase of the interfacial adhesion. The elastomeric particles can be observed within the PP domains and they remain

closely intact with these domains (Fig. 6).This is in agreement with Wang *et al.* (2003) results. Compared with Fig. 6 and Fig. 5, MAPP is much better coupler for the interfacial binding between WF and PP than MA-EPDM.

Conclusions

MA-PP and MA-EPDM, as compatibilizers in WF/PP composites, can improve the interfacial adhesion between wood flour and PP matrix. DMA analysis showed that the addition of compatibilizer decreased the loss factor of composites and improved the storage modulus, which had much better interfacial adhesion between the matrix and the filler than that without compatibilizer. Morphological feature studies showed that MA-PP and MA-EPDM improved the WF/PP adherence and the dispersion of the wood particles in the plastic matrix compared with the composites without compatibilizer, indicating a better interface adhesion. As compatibilizer of wood-flour/polypropylene composites, MA-PP was proved to be superior to MA-EPDM according to DMA analysis and SEM feature.

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